

Science Lectures

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PHOTOGRAPHY.

BY

CAPTAIN ABNEY, R.E., F.R.S.

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LECTURES TO SCIENCE TEACHERS.

PHOTOGRAPHY.

BY CAPT. ABNEY, R.E., F.R.S.

LECTURE I.

IN Fénélon's fables, under the title of *Voyage Supposé*, 1690, a visit to the Isle of Wonders is described, and in that book we read—

“There was no painter in that country, but if anybody wished to have the portrait of a friend, of a picture, a beautiful landscape, or of any other object, water was placed in great basins of gold or silver, and then the object desired to be painted was placed in front of that water. After a while the water froze and became a glass mirror, on which an ineffaceable image remained.”

Such was a fancy which, though then of a most improbable nature, presented itself to the mind of a French king's tutor some hundred years ago. In its broad aspect it became a reality when the first Daguerrean image was obtained; though accomplishment was, in a measure, effected in the early asphaltum prints of Niépce. It is with the realisation of this dream that we have to deal this morning; with that realisation which has furnished people, to be numbered by thousands, with the means of subsistence, and has created fortunes in some few instances; and which has put a new power into the hands of men of science in their investigations.

We shall only cast a rapid glance over the early history of photography, and endeavour to show as far as possible how it was that the great advances in it have been made.

In 1777 Scheele, of Stralsund, in Sweden, was the first who actually carried out investigations into the action of light on silver chloride. Before his time it was well known that "luna cornua" (as silver chloride was termed) blackened in the presence of light, but he arrived at the fact that a chemical change was brought about by the light. He found that silver chloride blackened by this agency on being treated with ammonia yielded up metallic silver, whilst if the exposure took place beneath water a soluble substance was separated, which, when silver nitrate was applied, gave fresh silver chloride. This was an important investigation, but no fruits resulted from it till many years later.

Wedgwood, in 1802, next called attention to photographic action, in a paper read before the Royal Institution, entitled, "An Account of a Method of Copying Paintings on Glass, and of making Profiles by the Agency of Light upon Nitrate of Silver," with Observations by H. Davy. This was the first published account of producing photographs.

Wedgwood used white leather or white paper as a substratum (using the former in preference to the latter) on which was brushed silver nitrate. In his paper he entered into details of his process, and admitted that the images so obtained could not be fixed or rendered permanent. Davy compared Wedgwood's results when using silver nitrate, with those obtained by silver chloride, and found that the latter compound was more susceptible to darkening by the action of light than the former; but in neither case could he fix the images.

The next eminent man who made essays on what we now call photography (or sun-writing) was Nicéphore de Niépce. He commenced his experiments in 1814, and in 1827 wished to communicate an account of them to the Royal Society of London; his paper was not received, owing to the details of the process being kept a secret. We now know that his process was founded on the action that light produced on bitumen of Judæa (more commonly known, perhaps, as asphaltum); he found that this body when exposed to light, became insoluble in the usual menstrua. Thus, if a thin coating were given to a metal plate and when dry exposed

in a camera to the action of light controlled by a lens, the part acted strongly upon by light would become insoluble, and thus when a solvent was applied (such as naphtha or petroleum) the shadows would be represented by the metal plate, whilst the lights would be formed of the dark resin. The image in this case would be reversed in the character of its shades, unless the black body could be whitened, and the metal blackened. After many experiments with this object in view, Nièpce applied *iodine to the image obtained with the asphaltum*. These bitumen pictures are still in existence, one or more being in the British Museum at the present time.

In 1824 Daguerre, who was devoted to painting, commenced similar experiments to those of Nièpce, each working in secrecy and unknown to the other. In 1826, however, through the want of reticence of an optician, who was an acquaintance of both, the fact that each of them was working in the same direction was learnt by the other, and in 1829 they entered into a kind of partnership. Here it may be that Daguerre first learnt the treatment of metallic plates with iodine, and watched the action that took place in the light, when silver was employed to receive the layer of asphaltum. At any rate to Daguerre belongs the discovery of the action of light on iodide of silver surfaces, and also the merit of producing a picture in the camera with but a short exposure. When I say short, I mean short compared with that given to the bitumen plates, for with such it took six or eight hours to obtain an image. Working with silver plates, which had been subjected to the vapour of iodine, he succeeded at first in obtaining visible images with prolonged exposure; but whilst endeavouring to obtain them in a moderate time he waded through endless experiments, and only chance befriended him at last. It thus occurred:—Having exposed some iodized plates in the camera and obtained no results, he placed them away in a cupboard containing a medley of chemicals. On opening it some time afterwards to procure an old plate to clean for fresh trial he found, much to his astonishment, one of them with a fully developed image upon it. I will not exhaust your patience by detailing how he traced the agency at work which had caused this development. Suffice it to say that it was found to be mercury (which vaporises at ordinary

temperatures) which had collected on the parts acted upon by light.

In June 1839 Daguerre's discovery was announced, and in August of the same year published to the world, and a pension of 6,000 francs per annum given to him by the French Government, whilst at the same time 4,000 francs was allotted to Niépce the Younger, who had succeeded to the partnership with Daguerre after the death of his uncle.

An outline of the daguerreotype process is as follows :—

A copper plate is silvered by the electro-plating process or any other convenient method, and after very careful cleaning, the silver surface is exposed in the dark to the action of iodine vapours. The iodine combines with the silver, and the metallic surface becomes covered with silver iodide, first canary coloured, then rose, then blue, and so on, *the colour being dependent on the thickness of the layer of silver iodide produced*. When canary-coloured it is supposed that the surface is in the best condition for receiving the impact of light.

It will now be convenient to point out the chemical change that really takes place in the ordinarily employed silver salts when exposed to the action of light. Under certain circumstances, when subject to its impact, silver iodide (which for our purpose we will call Ag_2I_2) throws off one atom of iodine, and we get subiodide of silver (Ag_2I), a slightly black body, left behind. Scheele proved by his experiments that silver chloride (Ag_2Cl_2), when acted upon by light, gave off chlorine (Cl), and we now know that the blackened product is sub-chloride of silver (Ag_2Cl).

Similarly, silver bromide (Ag_2Br_2) is converted into the sub-bromide (Ag_2Br).

Pure and dry silver chloride will change in the light. Pure and dry silver bromide will also change in the light, but not so readily as the chloride. *Pure and dry silver iodide is unaffected by light, unless any body which will take up iodine be present*; even moisture will induce the change if the impact of light be prolonged.

The sensitiveness of both the chloride and bromide is materially increased by the presence of any body which will absorb chlorine and bromine, and in all cases we may lay down the law that the greater its affinity for chlorine, bromine, or iodine, the greater the sensitiveness of the

silver-haloid. It should also be noted that however short the exposure to light may be, the same changes occur in a greater or less number of the molecules though such changes may be invisible to the eye, owing to the preponderance of the unaltered salts.

Now when Daguerre's plates were exposed in the camera for a short time, no visible image was apparent, but, nevertheless, some minute quantity of the Ag_2I_2 was converted into Ag_2I . It was found by Daguerre that such an invisible image had the power of condensing mercury from mercury vapour on the parts forming it, and that metallic lustre was given to it. Thus the Daguerrean image of this white piece of paper would have been represented by mercury and sub-iodide of silver, while this black piece of paper would have been represented by the silver iodide; and when the unaltered iodide is dissolved away, the latter would be represented by the dark-coloured silver, and the former by the lighter amalgam of silver and mercury.

I have here a glass plate silvered by Liebig's process, and we will place it for a couple of minutes in this common deal box,¹ at the bottom of which is a piece of cardboard which has been exposed to iodine vapour during the night. Iodine volatilizes at ordinary temperatures, so by leaving it in the box the surface will be converted into silver iodide by the combination between the metal and the halogen. I now withdraw it, and examining it by candle light, I find it of a delicate canary colour, with a slight tint of rose. It is now in a sensitive condition to ordinary light. I will not waste your time by exposing the plate in the camera, but will place it behind a glass negative picture (what that means we shall learn presently), and expose it for a few seconds in the beam of the electric light. I believe it is sufficiently exposed, so I will take it and hold it in the vapour coming from the mercury (heated over a Bunsen burner to about 150 F.) which is in this small capsule. The image begins to spring out at once, and after a little longer treatment it is fully developed. [The picture was handed round.]

Now silver iodide, as I said, is sensitive to light, that is, light changes it from the iodide to the sub-iodide so long as

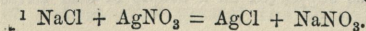
¹ The plate was supported on a couple of deal strips laid on the card.

some body is present which can take up the liberated iodine. What have we here, in this Daguerrean process, to do so? We have the metallic silver, for recollect that the iodide is only on the outer surface of the plate. Now I could demonstrate to you the fact that this silver is necessary had I the time. I might have repeated an old experiment, and, having silvered a similar glass plate, and converted the whole of the delicate metallic layer into silver iodide, have then shown its insensitiveness to light, owing to there being nothing to combine with the iodine, which it is anxious to liberate. I will show you by-and-bye another experiment which will illustrate the necessity of an absorbent.

Goddard, a countryman of ours, discovered that by treating the silver plate with bromine after the iodide had been formed, the exposure in the camera necessary to form a mercury-condensing image was shortened from minutes to seconds. Perhaps this was the greatest of all improvements in the daguerreotype process, as it rendered it thoroughly practicable.

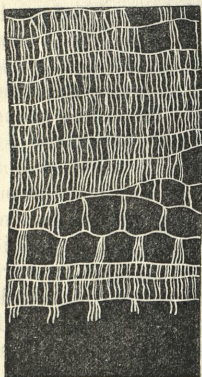
In 1834, whilst Daguerre was working in France on the production of sun pictures, Fox Talbot, a gentleman whom I am glad to say is still living, began experimenting with silver chloride, pursuing the same line of thought as Sir H. Davy, and in June 1839 (six months earlier than the publication of Daguerre's process) he read a paper at the Royal Society on photogenic drawing. This photogenic drawing is really the same photographic printing process that we employ now. Talbot impregnated writing-paper with common salt or sodium chloride, and when dry treated it with washes of silver nitrate, the result being to produce silver chloride¹ in the paper with a little pure silver nitrate ready to take up the chlorine which the darkening chloride would liberate. Ferns, leaves, lace, &c., he copied by this method; more than rivalling the draughtsman in accuracy and rapidity.

Let us suppose that one of the objects to be copied was a piece of black lace. When the lace was laid on the paper those parts beneath the cotton or thread would remain white whilst the ground would be blackened. The paper on the removal of the lace would represent the lace as *white* on a black ground. This picture Talbot termed a negative picture,



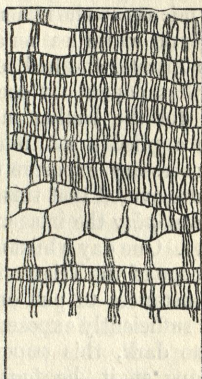
or, as it is now called, a negative. Such a blackened paper with the white image on it could be used to cover a second piece of sensitive paper, which on exposure to light would show the lace as black on a white ground; and this he termed a positive picture. Note the advantage of this process over the Daguerrean, which for each copy of an object required a fresh exposure in the camera.

Hitherto we have dealt exclusively with the method of



Negative.

FIG. 1.



Positive

FIG. 2.

producing silver iodide by the direct contact of the metal with the halogen; but the same results can be obtained by chemical decomposition. Silver iodide may be precipitated by mixing a solution of potassium iodide with silver nitrate.¹ This was the method adopted by Fox Talbot in the calotype process, patented in 1841. He added sufficient potassium iodide to a solution of the silver nitrate to precipitate silver iodide, and then an excess to redissolve it. Such a solution he brushed over a piece of paper, which when dry he washed, leaving on it primrose-coloured silver iodide. In this state the silver compound was insensitive to light, as there was nothing present (besides the paper) to take up iodine. We have here a piece of paper prepared as indicated, and it is now exposed to the strong glare of the

¹ $KI + AgNO_3 = AgI + KNO_3$.

electric light. To render it sensitive before exposure in the camera Talbot brushed over it a solution of silver nitrate and gallic acid, which I will get my assistant to do with our prepared paper. The gallic acid plays a most important part in the process, so much so indeed that I ought to mention that its utility was discovered previously to the Talbot-type process, by the Rev. J. B. Reade, a gentleman who but a few years since has passed away from amongst us. The method of his discovery was systematic. When securing images in the solar microscope he remembered that Wedgwood had produced images on white leather and paper on which had been brushed silver nitrate, and had found that his leather was more sensitive than paper. It occurred to Mr. Reade that the dressing used for the leather might have some important property, so he applied a solution of nutgalls to his paper, and found the necessary exposure to light was greatly shortened. He also discovered that this same nutgall solution had the power of *developing* the image. This, however, was a chance discovery. One day whilst engaged in producing photographically an image of the *Trientalis Europæa*, he was compelled through circumstances to put on one side the paper which had not been sufficiently exposed to give a visible impression. Placed in the dark, this paper was left till next day, when, on glancing at it, he found a perfectly distinct image. The gallic acid had played a part hitherto not dreamt of.

Reverting to the calotype process, we find that Fox Talbot employed the gallic acid with silver nitrate to render the paper sensitive (the former being what is termed an *accelerator*); and the discovery that an invisible image could be rendered visible by the same solutions was also utilised, for after exposure to the light the image was brought out by them.

Our own piece of Talbot-type paper is ready, it having been treated as indicated, and the excess of moisture blotted off on blotting paper. After placing it behind the same negative which we employed in illustrating the daguerreotype process, we will expose it to the beam of the electric light. A couple of seconds is a sufficient time to have produced an invisible image, and we will at once proceed to render it visible with a solution of gallic acid and nitrate of silver. This we dab on with a tuft of white wool, and the picture begins to appear. After a little patient manipulation the

whole of the details are brought out, and now we will place it in a dish of water for a while.

This operation of causing the invisible to become visible, how is it effected? We must set ourselves to solve the problem by referring to a kindred action. If a rod of zinc be placed in a strong solution of acetate of lead, by degrees this latter becomes decomposed, and crystals of lead deposit on the rod and completely cover it; but the action does not cease when the covering is effected: the lead solution still keeps depositing the metal, and a beautiful network of leaves formed by metallic crystals is built up. The first particles of lead deposited on the zinc attract other particles from the solution till we have what is known as a lead-tree.

In the development of the image, as our last operation is called, we have simply an example of the laws of crystallisation, like crystals tending to adhere to like, and to be attracted by them. Now in our exposed paper we had some excessively minute portions of silver iodide (Ag_2I_2) reduced to the state of sub-iodide (Ag_2I). Only one silver atom of these more elementary molecules is saturated as it were, and the other is free, and it is this free atom that is capable of attracting metallic silver from a solution of silver nitrate, when this latter is in an unstable state. In the present instance the instability is caused by the gallic acid, for this body tends to absorb oxygen, and as it absorbs oxygen it liberates from the silver nitrate the metallic silver, and as quickly as the separation is effected the free silver atoms attract it. We thus get an image built up on the sub-iodide; for after one small particle of silver has been attracted, it, in its turn, attracts others, as in the case of the lead in the lead-tree. This then is the secret of development; it is the attraction exercised by the sub-iodide for freshly-separated silver.

The developed image is therefore a metallic image; but in order to render it permanent, or perhaps I ought to say, more clear, it was necessary to get rid of all the silver iodide. To Sir J. Herschel belongs the discovery (in 1819) of the solvent property of sodium hyposulphite on the silver chloride, and it was by the application of this salt to the iodide that the desired fixing of the image was effected. It is a matter of surprise that this solvent was not employed at an earlier date.

We will now take from the water our developed print and fix it in a solution of sodium hyposulphite; after washing it will be permanent, or nearly so.

Ten years after the patenting of the calotype by Fox Talbot, a new era arrived in photography. In 1851 was published the collodion process—a process which we use to the present day, and one which there seems to be no chance of superseding, at all events for ordinary work. In the calotype pictures the surface of the paper was found to be too rough to render fine details, and at an early period of experimental photography Sir J. Herschel had suggested the employment of glass as a substitute, and in fact himself had produced pictures on it, for in our Exhibition we find such a picture taken as early as 1839. The method he adopted was to obtain a fine precipitate of silver chloride in water, and at the bottom of the containing vessel to place a glass plate. After a lapse of some time the chloride was deposited with sufficient solidity to render it practicable to remove the glass from the vessel. After flowing over the crust of silver chloride a little silver nitrate he allowed it to dry, and exposed the plate in the camera. The picture I hand round was produced in this manner.

At a later date Nièpce de St. Victor went a step further and employed a film of albumen for holding the sensitive salts of silver *in situ* on glass—an example of an early picture so produced is in the Exhibition; but to Le Gray belongs the honour of suggesting *collodion* as a vehicle to attain the same end. Archer, with whom was associated Dr. Hugh Diamond, however, practically introduced it.

Collodion is a solution of gun-cotton in ether and alcohol, and when properly prepared should leave a transparent film when the solvents evaporate. The iodides, bromides, and chlorides of the alkalis, and also of many of the metals, are soluble in alcohol, and can therefore be introduced into the collodion, and be left in a film of this viscid body when poured over a glass plate. A mere outline of the collodion process is as follows:—A plate is coated with collodion containing an iodide and bromide, as I do this one [shows], and when the ether has evaporated and the film is “set” or become gelatinous, I place it in a dish containing a seven per cent. solution of silver nitrate. On looking at the plate I see the silver compound gradually forming, and after the lapse of about a

minute the film seems nearly opaque. I take our negative picture, and, at each end of it lay a very thin strip of glass and place the sensitive plate upon them. (The strips of glass are used to prevent the surface of the collodion film being abraded by contact with the other plate.) I expose to the electric light for a second. On removing the plate I can see no trace of an image, but I will endeavour to show you its development.

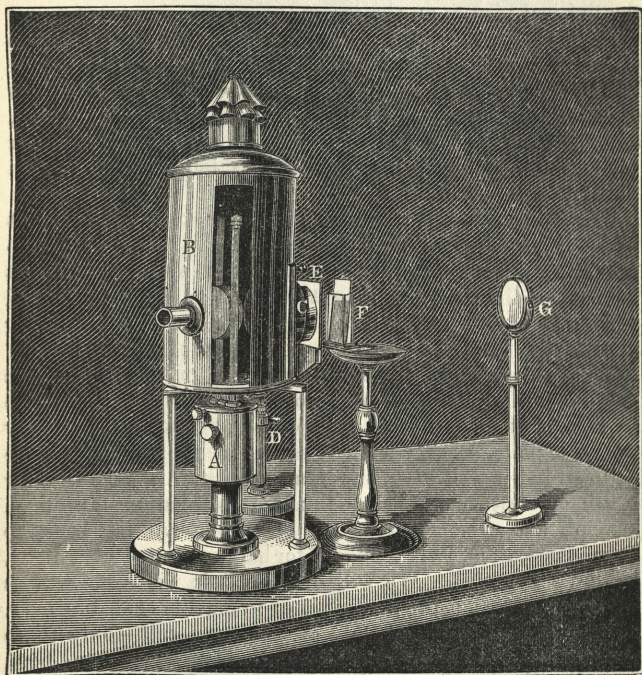


FIG. 3.

Close to the lens (C) of the lantern (B) of the electric light (A) I place a piece of red glass (E) in the clamp (D), for reasons which subsequently will be apparent to you, and immediately in front of that a glass cell (F) containing a solution of ferrous sulphate slightly acidified with acetic acid. I now

use a lens (G) to form an image of the cell on the screen. This being arranged, I dip the glass plate into the solution. You see at first not a sign of any image, but only a semi-opaque film. But now we see a darkening in parts, and a picture is gradually appearing. It gains intensity, and now it is perfect in all its details. We will withdraw it and wash it, and then treat it with a little potassium cyanide, which is also a solvent of many of the compounds of silver. After washing again we will place it in the lantern and throw the finished picture on the screen.

Here then we have a picture produced by the collodion process. You will have noticed that this time the image was brought out by a solution of ferrous sulphate and not of gallic acid. Ferrous sulphate is a greedy absorber of oxygen, and therefore is effective in causing a reduction of silver from the nitrate, with which the plate was impregnated before placing in the cell.

We are now in a position, I think, to make an experiment which I promised at an earlier part of the lecture, viz., to prove to you that silver iodide is unaltered by light unless it has some iodine-absorber present with it. In my hand I hold a glass plate to which is adhering a collodion film containing pure silver iodide and having no excess of silver nitrate. After placing it in the direct rays of the beam from the electric light, I apply a solution of pyrogallic acid and silver nitrate to it, and there is no change apparent. Taking a similarly prepared plate, I apply a small square piece of silver leaf to it, brushing it well on to the film. With this camel's hair brush on another portion I brush a solution of tannin in alcohol, and after warming the glass through its back to cause desiccation, I will expose it for half a minute to the light, behind a negative. We will develop it in the same way as our last picture, using a solution of pyrogallic acid, however, instead of ferrous sulphate. Notice the result—only those portions of the negative appear on our plate which have been coated with the silver or have received the wash of tannin. After fixing our picture I throw it on the screen, and we see our results more perfectly. The transparent parts through which the light passes show where the actinic rays did not affect the silver iodide.

You will notice that the part A is somewhat fainter than B. The former you will recollect was the part on which was

placed the silver leaf, whilst to B was applied the tannin. The reason of the difference is obvious. It is only those particles of the silver iodide in actual contact with the iodine-absorber which can be affected by the light. In the

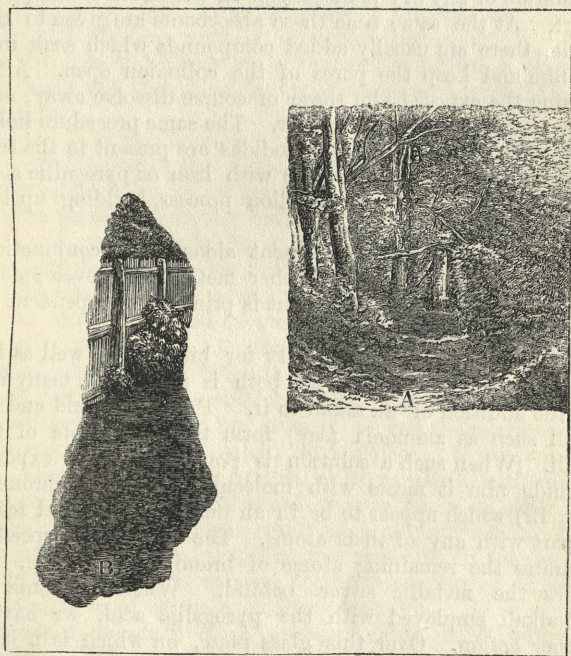


FIG. 4.

one case the silver leaf was only in contact with the surface particles, in the other the tannin permeated the film. Having thus prepared the ground, we are in a position to understand the preparation of dry plates, as they are called, that is, the preparation of sensitive films in collodion which can be exposed in the dry state.

If a surface of silver iodide were allowed to dry with the free silver nitrate solution from the bath upon it, the latter would crystallize and spoil the film. If we wash away the free silver nitrate it would be insensitive, but if

in its place we applied some iodine absorbent (*after washing*) which is less crystallizable, such as tannin (as we did in our last experiment), salicin, tea, coffee, &c., it will again be sensitive even when dry. The application of such bodies is the foundation of any dry plate process in which the iodide plays a part. At the same time these absorbents are given to the iodide, there are usually added compounds which soak into the film and keep the pores of the collodion open. After washing the exposed film these of course dissolve away, and allow free access to the developer. The same procedure holds good when *both* bromides and iodides are present in the sensitive film, and we may develop with iron or pyrogallie acid and silver, as in the wet collodion process, building up the image on the irritated haloids.

When silver bromide is present alone, or in conjunction with the iodide, however, another method of development may be resorted to, viz., one that is primarily independent of the *deposition* of metallic silver.

Pyrogallie acid has an affinity for bromine as well as for oxygen, and the affinity for both is multiplied manyfold by the addition of an alkali to it. Pyrogallie acid and an alkali such as ammonia (say) form the pyrogallate of the alkali. When such a solution is poured over the exposed bromide film it meets with molecules of the sub-bromide ($\text{Ag}_2 \text{Br}$) which appear to be in an unstable state, and ready to part with any of their atoms. The pyrogallate speedily separates the remaining atoms of bromine from them, and leaves the metallic silver behind. When ammonia is the alkali employed with the pyrogallie acid, we have a further action. Over this glass plate, on which is a layer of silver bromide in collodion, I allow a few drops of strong ammonia to trickle. Notice the transparent track they leave. From this we learn that the bromide is soluble in ammonia. Hence, whilst the pyrogallate is still acting in the manner indicated, if there be sufficient ammonia present it dissolves a portion of the silver bromide; this the pyrogallate decomposes, and causes the metal to deposit as in the ordinary development. By this means a greater density is given to the image than would otherwise exist. There is a further density given by a somewhat curious action (apparently catalectic) the cause of which I have not time to explain.

I should state that sometimes the avidity of the pyrogalllic acid in the presence of ammonia for bromine is so great that it is found necessary to give it a soluble bromide wherewith to satisfy it. Thus potassium bromide is usually added to the alkaline developer. We will expose a plate prepared with silver bromide behind a negative and develop it by this alkaline method, throwing the resulting picture on the screen. There is no noticeable difference between this image and that developed with the ferrous sulphate in the wet plate.

Now it is not necessary to prepare a sensitive bromide film by immersing the collodionized plate in a solution of silver nitrate; by an artifice we can have the sensitive salts held in suspension in the viscid collodion.

I will very briefly carry you through the operations necessary to produce this emulsion, as it is technically called, of silver bromide. In collodion are dissolved soluble bromides. Silver nitrate dissolved in weak alcohol is added in sufficient quantity to convert it into silver bromide. If rightly carried out, this solid bromide remains in suspension in a very finely divided state in the collodion. The collodion is next poured out into a dish and allowed to become gelatinous by the evaporation of the ether, after which it is well washed (to eliminate all the soluble salts present), and dried. The pellicle is next redissolved in a mixture of ether and alcohol, and we have as a result such a viscous fluid as in this bottle. To prepare a film for exposure in the camera, all that is necessary is to pour it over the surface of a glass or other plate as if it were ordinary collodion. It is equally well acted on when dried as when still moist with the solvents. It is usual to add some bromine absorber to the collodion, but this is not absolutely necessary, though it is generally considered that sensitiveness is increased by so doing.

LECTURE II.

WE left off with the development of the dry plate by the method known as the alkaline process, and this morning we must break into new ground. But yesterday after the lecture a gentleman came to me, and said, "You have not spoken about the latent image." Now what is called the latent image is a thing I hesitate to recognise. I will admit there is an invisible image, but not what should strictly be called a latent image. If we take 10,000 parts of oxide of zinc, say, and mix thoroughly with it one part of lamp-black, you will perceive no difference in tint between the pure oxide of zinc and that contaminated with the lamp-black; but the lampblack is there nevertheless. So in the same way when we expose for a short time a sensitive plate to the action of light, a change has taken place in certain molecules exactly in the way that would give us a visible image by a longer exposure, the only difference between the one and the other being in the quantity of molecules affected. I think I need scarcely repeat the experiments which showed the development of the invisible image. Suffice it to say that the visible as well as the invisible image, can attract silver from an unstable solution of silver nitrate.

But to-day we have to consider as to the light which is most favourable for photographers, *i.e.* to what rays of light these salts of silver are most sensitive. If you cause a slice of white light to pass through a prism, it is separated into its component rays, and we have what we all know as the spectrum. The spectrum of the light from the incandescent carbons is now thrown on the screen, and if I were to place a large piece of paper impregnated with a sensitive silver salt such as the iodide in that spectrum—and I have taken the iodide with a set purpose—we should notice, on the application of a developing agent, that no change in its molecules had been effected by the red and yellow rays, but that green, blue, violet, and the invisible rays beyond the violet

had been active. The length of the ultra-violet part of the spectrum is equal in length to the whole of the visible spectrum. Mr. Lockyer and Professor Stokes, I think, have told you about these ultra-violet rays, and I am not going to repeat what they have said. Instead of using the electric light we may pass a very thin slice of sunlight through a prism or a couple of prisms, and when we do so, we find a spectrum traversed by black lines, which you have already heard are due to the absorption of metallic and other vapours. Those lines, as you are aware, occupy certain fixed positions in the spectrum, and supposing that we get photographic impressions bounded by any particular line, we should know what part of the spectrum was effective.

Before proceeding further I may show you that with the ordinary silver salts employed the red light is inoperative to produce a picture, whilst the blue light is perfectly capable of so doing. I have here a dry plate prepared with bromo-iodide of silver (I told you yesterday that we mixed bromides with iodides in the collodion, and produced silver bromo-iodide in the film by means of a solution of silver nitrate), and I will expose, for a minute, one half of it behind a negative to the red rays, and the other half for ten seconds to the violet rays. You will see that in the first half of the picture we shall get no results, and in the other half we shall get an image. After it is developed I will throw it on the screen. Here it is after the developer has been applied, and you see the red light is incapable of impressing an image. Before I came yesterday I photographed the spectrum on different silver compounds, to show what rays are capable of producing an image, and when you compare this photograph, taken on the iodide salt, with the carefully coloured drawing hanging on the wall, you will find what I told you was correct about the silver iodide. [The photograph shown on the screen.] The transparent line, which you see at the extreme end of the image, agrees with the line E of the solar spectrum, and when we turn the light on the diagram of the spectrum you will see what position this line occupies in the green. The spectrum goes along through the blue, through the violet, and here we get two well-known lines, called the H lines, also to be seen in the diagram, which are very near the extreme end of the violet portion. You can now see that the photographic action goes far beyond them,

right into those portions which are usually invisible. To obtain this photograph and those which I shall show you directly, the spectrum was thrown on the sensitive compound after passing through ordinary glass prisms and glass lenses. If I had employed quartz lenses and prisms, or Iceland spar lenses and prisms, I should have been able to obtain an impression much further in the ultra-violet, because glass cuts off these rays to a great extent; but as photographers use glass objectives, I thought it best to show you the spectra as produced through this medium.

I now wish you to compare the spectrum when photographed on other silver compounds, with that already shown. You will notice that the iodide shows the greatest impressibility to those rays which correspond to G, whose wave-length answers to about $4,300\frac{1}{10^{10}}$ metres,¹ at which point it seems to tumble down a precipice in the direction of the violet. The lowest ray which effects it is the E, which corresponds to about 5,200. The maximum effect produced on the bromide seems to take place at about the same wave-length and to diminish more gradually and regularly in both directions. On the chloride the intensity seems to be nearly of the same character as that of the iodide, though the fall in effectiveness is not so marked towards the H line. We may say, then, the gradients of the sensitiveness of the bromide to the spectrum are far less steep than those of the iodide and chloride. The question comes, then, is it not possible to have some compound which shall give a gentler gradient than the bromide, and thus enable us to photograph further in both directions, or, if that be not possible, cannot we change the point of maximum effect to a point nearer towards the red end, by employing a different silver compound, and yet preserve the same gradient, as the bromide? In either case we should be able to photograph further down towards the A line.

Each ray of light, as you doubtless are aware, is caused by a different vibratory motion of the all-space-pervading ether. The waves producing the red rays are longer than those producing the orange, the orange than the green, and so on. Now

¹ In future we shall refer all these wave-lengths to the same scale of $\frac{1}{10^{10}}$ metres.

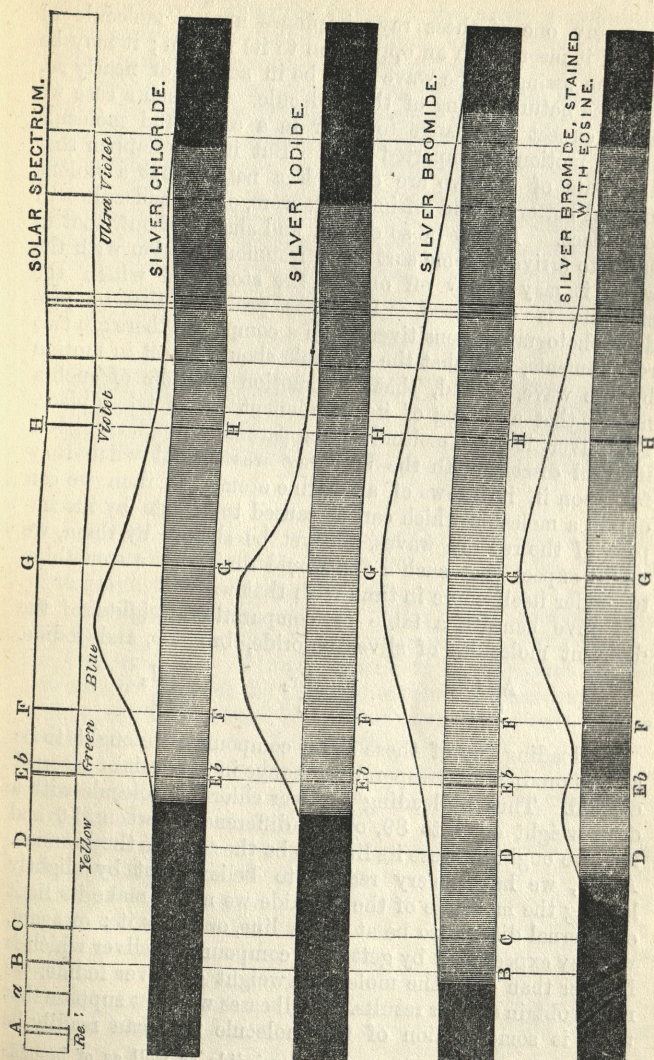


FIG. 5.

when any one of these rays impinges upon a molecule of matter, it meets with an opposition to its motion; it may be that the swing of the wave may be in accord, or nearly so, with the natural swing of the molecule. In such a case we might expect no change to occur in a compound molecule though motion be imparted to it. But it may happen that the beats of the two are of such a nature that a violent internal battering and sifting, as it were, of the molecule will take place. It may be so driven and shaken about, that in order to arrive at some sort of harmonious motion with the wave, it may throw off one of the atoms of which the molecule is composed. It seems probable that to produce photographic sensitiveness in a compound there are two requirements, first, that the molecule should be set in motion by the wave, second, that the motion must be of such a nature that a sifting of its component atoms takes place. The silver iodide¹ molecule is apparently in the greatest internal discord with the blue ray waves, and when they fall upon it, it throws off an iodine atom. If then we can obtain a molecule which can be caused to vibrate by the impact of the red ray waves, and yet be shaken by them, we might expect that such a one would throw off a something to render itself more in tune with that wave.

I give beneath a table of comparative weights of the different molecules of silver chloride, bromide, and iodide.

Ag_2Cl_2	Ag_2Br_2	Ag_2I_2
287	376	470

By loading any of these silver compounds we ought to be able to produce a corresponding change in the limit of internal discord. Thus by loading a silver chloride molecule with a dead weight equal to 89, or the difference between 376 and 287, we ought to cause its limit to be the same as the bromide. Again, we have every reason to believe that by slightly loading the molecule of the bromide we might make its limit of internal discord to be at the A line, or below it; or again, we may expect that by getting a compound of silver which is heavier than 470, the molecular weight of silver iodide, we might obtain similar results. In all cases we must suppose that there is some portion of the molecule that can readily be

¹ The absorption spectrum of silver iodide as well as of bromide shows the greatest absorption to take place in the blue.

shaken off by it when the swing of the wave is sufficiently inharmonious. It should be noted, however, that in these loaded molecules the increased weight may be a dead weight, as it were; that is, the part shaken off may still be chlorine, iodine, or bromine, if the compound contain any or all of these halogens. I now throw on the screen a photograph of the spectrum taken on loaded silver bromide. The bright line in the centre is the extreme limit of visibility, the A line; on the left beyond the A line there are indications of bands of lines, and when you come to examine microscopically a good photograph, you can see that it is particularly rich in lines, a great many of which are due to the absorption of the atmosphere.

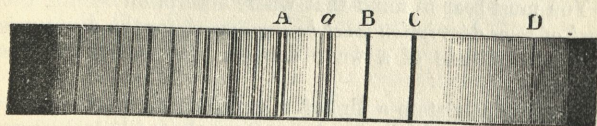


FIG. 6.

To show you that it is not only the solar spectrum that can be photographed by this means, I have here the first photograph taken by myself of the red end of a spectrum of a metal, namely, of calcium. This metal is particularly rich in red rays, together with some rays beyond the extreme limit of visibility. I may remark in passing that by the process here adopted the point of maximum photographic intensity in the spectrum is lowered towards the red. Those two black lines on the left are the last which can be seen, and the lines towards the right lie beyond the A line. Their waves are of such a length that they cannot impress themselves on the nerves of the eye.

I should like to expose a plate coated with this sensitive salt, to show you that there is no illusion about photographing with red rays. I have here such a one which I will expose to the red light only; it will require perhaps a minute's exposure, and I must have it developed as far as possible in the dark, otherwise the image would be veiled. [The developed image was then thrown on the screen.]

Dr. Vogel, of Berlin, has experimented with bromide plates prepared in the silver bath, which, after washing, he flooded with various diluted dyes. He has found and often

correctly, that the film becomes sensitive to the action of those rays which the dyes will absorb. Blue, however, according to his theory, should absorb all the red rays, and thus be chiefly sensitive to the red and yellow. Experiment does not always bear him out in this. I am inclined to think that by the use of these dyes he forms a real compound with silver (for however well you may wash your plates you cannot eliminate all free nitrate of silver), and thus loads his molecules. To explain Vogel's reasoning I will throw the spectrum on the screen, and place a glass cell containing eosine dissolved in alcohol before it; you see there is an absorption in the green, whilst the fluid allows the rays immediately above and below it to pass.

You must bear in mind that where absorption occurs, there *work of some description must be performed*, for the diminution of the amplitude of a wave denotes that energy has been expended.

If we faintly stain a film of silver bromide with eosine, so that the dye absorbs the green rays through its whole thickness, and carries, as it were, the light to every individual molecule in its path, the rays not so rapidly absorbed should not cause such a rapid chemical change. By increasing the strength of the dye on the *washed* plate it is possible to prevent any change in the portion exposed to the green rays, as they are absorbed before they get to the bromide, but if at the same time we increase the silver in the film to such an extent as to allow the whole of the dye to form a compound with it, the effect is still more marked. By this procedure I have been enabled to photograph below the "a" line, with the weighted molecule of bromide. I throw on the screen a spectrum taken on a plate slightly stained with eosine (see Fig. 5), and I will ask you to compare it with the absorption spectrum of the dye and also with the spectra impressed on the other silver compounds. As I said before, I believe that the results obtained with the dyes by Vogel are due to their combination with the residue of silver nitrate left in the film, and what seems to tend to confirm this view is that if the film contain excess of soluble bromide, no results are to be obtained.

Dr. Vogel's researches do not absolutely point to obtaining a method of prolonging the photographic spectrum, yet they tend towards it. You must not accept my explana-

tion of them as correct (though I believe it to be so), as the theory is still in the course of examination by Dr. Vogel, Captain Waterhouse, myself, and others.

We must again travel forward a step, and now we shall find it more easy to understand the production of photographs of a certain kind which we find in the Exhibition. If we take pure silver chloride and expose it to the action of the spectrum sufficiently long to give a visible impression, we find that it extends from the green to far beyond the extreme violet, but that no action takes place in the red. I exhibit here a photograph of the spectrum taken on paper impregnated with silver chloride; the exposure necessary to produce this print was three-quarters of an hour. Another similar piece of paper was taken and slightly darkened in diffused light, and placed in the spectrum. The impression of the blue rays continued, and at the same time there was a browning action taking place where the yellow rays were thrown, whilst at the extremity of the red a decided pink was apparent. Two such spectra I have here, one fixed and the other not fixed; you will perceive that in the former the red tint has been lost, though there is an evidence of decided darkening beyond that due to tint on the paper. In the latter the colours are still extant.

Now conjointly with these results I wish to bring to your notice another experiment that any of you possessing a prism, and a camera, and a looking-glass can repeat, if you have even the smallest photographic knowledge. Take a glass plate and prepare it as if you were going to take a picture, expose it to the daylight and develop it, then "intensify" till you have a perfectly opaque film of silver, and dissolve away the unaltered silver salts, and wash well. Next take some copper chloride and flood the film with it. It will gradually seem to turn to a dirty white by reflected light, and by transmitted light it will be a reddish brown, for the copper will part with half its chlorine to the silver, which there is every reason to think is converted into a mixture of chloride and sub-chloride. Now expose such a plate to the action of the spectrum for ten minutes. You will find that where the violet, blue, and green rays come, you have a darkening of the surface, whilst where the yellow and red rays fall you have a bleaching action.

Again, take another plate, similarly prepared, but give

it a final wash with silver nitrate, and allow it to darken in white light, and then expose it to the spectrum, or beneath red, green, yellow, and blue glasses. In this case we shall find the silver reddens in the red light, becomes greenish in the green, and blue in the blue. I have here a plate that has been so treated and exposed to the different coloured lights, and you can note the colours though they are somewhat spoilt by subsequent experiments. Mark the difference between the two plates: one had a chloride and sub-chloride of silver alone, the other had chloride, sub-chloride, and a chlorine absorbent present.

We may class the result obtained on the silver chloride on paper and that on the last coloured plate as identical, both being exposed under the same conditions. Leaving out, for the present, the theory of the production of the colour, let us examine the fact that a change has been effected by the rays of low refrangibility. We have silver chloride and sub-chloride together in close contact on the surface, and I think we may take it that we have the case of a loaded molecule, whose swing is in discord with the longer waves; that such a discord causes an atom of chlorine to be thrown off (as before explained), and that the atom so separated is from the portion of the compound molecule which by itself would be the sub-chloride. As a result of the impact of the light we should have remaining metallic silver (from the sub-chloride) and unaltered silver chloride. The amount of sub-chloride formed by the preliminary exposure would be small, hence the total amount of reduced silver would be little in comparison with that which would be due to the reduction of the chloride to the sub-chloride by the more refrangible portion of the spectrum. The well-known reversal of the lines of the red end when photographed on iodide or bromide of silver, to which a slight preliminary exposure has been given, can be accounted for in the same way, on the supposition that the silver reduced from the sub-iodide or bromide is not so actively attractive as the sub-iodide or sub-bromide itself. The fact that such reversed photographs are always more or less veiled is rather confirmatory of this view.

With the plate treated with copper chloride alone, and no subsequent addition of silver nitrate and preliminary exposure, the same line of argument still holds good. Part of the sub-chloride is reduced to silver, and chlorine is evolved, the latter

being absorbed by another portion of the sub-chloride, with which it combines to form the white chloride. The minute atoms of reduced silver are shrouded by its whiteness, and we have the consequent appearance of the bleaching of the brownish-coloured film.

The cause of the colours in the paper-print and in the plate requires explanation. The fact that when the unaltered compounds on either of them are dissolved away, the colour vanishes, leaving only that due to silver itself throws a light on the subject.

In a soap bubble the beautiful colours which overspread its surface are caused by the interference of the light reflected from the outer and inner surfaces which are microscopically near each other, and it may be that the colours produced by the spectrum are the results of the interference of the light reflected from the surface of the reduced particles which are held apart by intervening silver chloride.¹ After dissolving out the latter, the particles are brought in contact and the colour disappears.

In the Exhibition we have photographs in colour, representing the solar spectrum, by Becquerel, and one of my objects in leading up so far as I have was to try and give you an explanation of the method of their production. On a bright silver surface silver sub-chloride was formed by voltaic or other means, and a spectrum was caused to fall on a plate so prepared imprinting itself in all its colours. If exposed to the light these spectra fade away and leave nothing behind but a bluish brown plate. Hence it is that they are preserved in closed light-tight cases, and can only be rarely exhibited.

The cause of an action taking place by the impact of the red and yellow rays has already been pointed out; and the vividness of the colours can also be readily accounted for by the same explanation as given to account for those on our paper and collodion film, when it is remembered that there is the reflecting surface of the silver plate itself to aid the interference.

Hitherto we have only spoken about silver compounds being sensitive to light, but nearly all matter is sensitive in one respect or another. Most probably the first action

¹ Silver chloride is really a white transparent substance, as may be proved by fuzing it in a crucible.

with which man was acquainted as photographic action was that of the tanning due to the sun, and in very primitive days no doubt it was more marked than it would be at the present day. The next change most probably would be noticed by the fair sex, who used coloured materials for their dresses, and ladies soon found out that silks, calicoes, or ribbons of certain colours materially changed under the action of light. Here I have three pieces of different coloured materials on which you are able to produce an image by the fading of the dyes. These have been exposed under a negative to the action of light, not heat. The usual explanation about the fading of these colours is that there is something given off like the scent from a rose; but when you see a map absolutely printed by light on them, you can have no doubt as to the action which has produced it. If it were that a sort of essence is given off, a negative placed over these colours whilst in the light would produce no defined result whatever, they would fade equally under it; we therefore cannot help concluding that some chemical change has taken place. Again, you will find most unlikely substances, such as glass, change under the influence of light. My friend Mr. Dallmeyer has some beautiful specimens of glass, which have been altered in this way; flint glass being changed to a yellow colour and crown glass to a purple tint. Again, we know that there are elements which are affected by light, and amongst them I may mention selenium, a body whose resistance to the passage of a current of electricity it has been proved is diminished by the impact of light. Thus in darkness a piece of selenium $1\cdot5$ in. \times $\cdot5$ in. \times $\cdot05$ in. offered 333000 units of resistance to the passage of the current. Whilst in the diffused light it offered nearly 270000 units. It was also found that the resistance was decreased most in the least refrangible portion of the visible spectrum. In the blue it was only 279000 units, in the yellow 277000 units, and in the red 255000 units of electrical resistance. I have brought this forward to show to you that a simple elementary body may be acted upon by light.

We also find that the colouring matter of flowers and of leaves is affected by light. Mrs. Somerville and Sir John Herschel made a long series of experiments with it. If you take the leaves, say, of common cabbage, and place them in alcohol, a certain coloured resin is extracted, which is known

by the name of chlorophyll. Its solution is red by transmitted, and green by reflected light. Here we have a piece of paper which has been brushed over with this alcoholic solution : the colour is a sort of primrose green. By exposure to light it has become bleached. This bleaching is principally due to the yellow light and not to the blue light, which acts on the salts of silver. Again, if you take the leaves of stocks, common wallflowers, violets, or roses, and treat them with alcohol, you can extract the colouring matter, and if, having brushed it over, you expose it beneath a negative, you will get prints of various colours. If you treat the rose extract with a small quantity of acid and brush it over a sheet of paper and expose it to the light, you will find the natural pink colour intensified and the subsequent change will be increased. Again, take the common violet, treat its extract with ammonia, and it gives you a green solution, but the green colouring matter is bleached by the action of light, and experiment proves that the parts of the spectrum to which the colouring matter is sensitive are not the same as those to which the silver salts are sensitive. There is a wide range of experimental work yet to be undertaken with respect to this colouring matter of flowers.

I should here like to call your attention to the fact that some gaseous bodies as well as solids are affected by light. If, for example, we take hydrogen and chlorine in proper proportions in a glass bulb, and keep them in the dark, no combination takes place ; but if we take such a bulb into sunlight, they combine almost instantaneously, the light causing the atoms to swing in such a way that they mutually attract each other, and form hydrochloric acid. As Dr. Tyndall has shown, it is not heat-waves that cause the atoms to combine, but light-waves ; he enclosed the gases in a collodion balloon, and then caused them to combine by a concentrated light, and the film was found unburnt. In diffused light the combination takes place slowly and without explosion. For similar reasons, if chlorine be passed into water in the daylight, hydrogen is abstracted from the water and hydrochloric acid is formed, the oxygen forming another compound with the chlorine.

The bodies to which I next shall call your attention as sensitive are metallic compounds. Sir John Herschel was the first to investigate the action of light on iron com-

pounds, and to him are due a variety of most interesting processes, examples of one or two of which I shall endeavour to show you.

Whilst mentioning the above great philosopher, I should like to point out to you the instrument with which he operated when experimenting on the effect that light produced on different organic and metallic compounds.

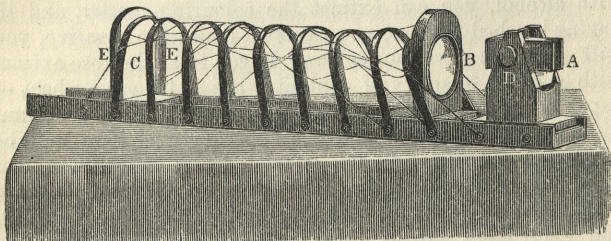


FIG. 7.

A is a glass prism which could be rotated in its frame round an axis D, so that the sun's rays would be dispersed in any given direction. B is a lens defining the spectrum (which, it must be recollected, was a mixed one, and not pure). C the screen on which the spectrum was raised, and on which the compound to be tried was placed. At E was marked a line on which one particular part of the spectrum was invariably caused to fall. When used the frame-work was covered with a black velvet cloth. The absolute results of the experiments on the different compounds are shown in an old book containing a list of Fellows of the Royal Society, over whose distinguished names they have been pasted. This book is perhaps one of the most interesting exhibits in the Loan Collection.

Reverting to the iron salts I may point out that those of them which are in the ferric state are the most readily acted upon by light; the ferrous salts, as a rule, not being sensitive. A variety of ferric salts may be formed, such as ferric chloride, or ferric oxalate; or you may have a compound of ferric citrate with citrate of ammonia, and so on. Of all the compounds of iron, Sir John Herschel found that this latter ferric salt, when employed with the ammonium citrate,

was the most easily operated upon. If we take a piece of paper and brush over it a mixed solution of these two salts, and when dry expose it to light beneath a negative for a short time (about two minutes), we shall obtain a blue image after treating it with a solution of potassium ferri-cyanide. This blue colour can only result from the contact of the potassium ferri-cyanide with some ferrous compound. Here then we have a demonstration of the change effected by light; the ferric compound is reduced to a ferrous state.

I will endeavour to produce such a print before you, but I must tell you that these iron salts are most objectionable for lecture experiments. If you expose a piece of paper which has been coated with this ferric compound, causing an image to be formed of a ferrous salt, and put it away in the dark, it rapidly loses the impression altogether. The ferrous becomes reconverted into the ferric salt. This is exceedingly tantalizing. I had some sheets of prepared paper exposed only this morning, and on developing them by the method already indicated, you see the image is very weak, due to this reactionary cause; had it remained undeveloped a few hours longer we should have had no image at all.

An iron print can also be developed by means of silver nitrate. A ferrous salt of iron will reduce silver nitrate to its metallic state, as already shown in yesterday's lecture; and if I bring a solution of the latter on to the exposed print, you will see that the silver deposits on those parts affected by light.

The next salts to which I must call your attention are the uranium salts, of which there are specimens on the card which you see before you. Uranium nitrate is sensitive to light in the presence of organic matter, being thus reduced to the state of an oxide. This oxide precipitates silver and other metals from their solutions, and with potassium ferri-cyanide forms a nearly insoluble brown compound.

We will now develop a picture with the ferri-cyanide, and you will note its appearance. I have also another photograph printed with uranium, which is now being placed in a solution of silver nitrate, to which a little gallic acid has been added. The silver is gradually being reduced by uranium oxide, and a metallic image is being built up. After passing the paper through sodium hyposulphite and washing, the picture is permanent.

The other most interesting compounds to which I would call your attention are those of vanadium. Professor Roscoe found, during some recent researches, that certain vanadium salts were sensitive to light. Here is the first vanadium print ever produced. It was developed by silver nitrate in a manner similar to that employed with the uranium print.

I am obliged to pass over some other metallic compounds, but I must mention the potassium dichromate, or rather the chromium salts. These salts are the great handmaidens of photographic printing processes at the present day. When you brush a solution of potassium dichromate over paper and expose it to the light, you will find the paper becomes darkened where the light has acted, and an oxide of chromium has been formed, the organic matter in the paper having reduced the potassium dichromate to that state. I have here such a piece of paper which has been exposed under a negative, and washed afterwards; and you see the green coloration of the chromium oxide.

Not only is the potassium dichromate reduced to the state

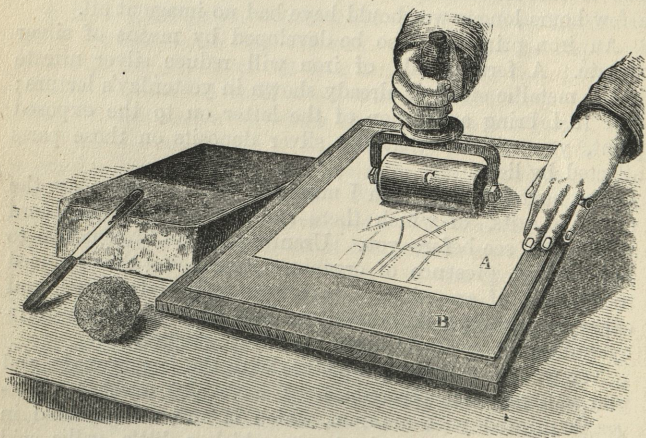


FIG. 8.

of oxide, but it also oxidises the organic matter with which it is in contact. If you take gelatine or any similar colloid body and add to it a solution of potassium dichromate, dry

it, and expose it to the light, you will find the gelatine has undergone a distinct change. First of all, the gelatine has become insoluble in hot or cold water, and in the second place it has become incapable of absorbing water. I have here a sheet of paper (A) coated with gelatine, in which was dissolved potassium dichromate. It has been exposed to light under a negative of a map, and, as I have just told you, it will not absorb water where the lines are printed.

I immerse it in water, place it on this glass plate (B), blot off the excess of moisture, and then roll it with this roller (C), which has been charged with greasy ink. The ink is already beginning to take on the lines; I run the roller briskly over it once or twice to give more ink to them and to remove any adhering superficially, and we have now got a finished map whose lines are formed of the greasy ink; this process of reproducing plans I have called the papyrotype process.

In a simple way I want to show you also that gelatine becomes insoluble in hot water by the action of light when it is in contact with potassium dichromate. I have here a piece of gelatinous paper, which has been exposed under the same negative as before, its surface whilst dry has been covered with a thin layer of greasy ink. Now if gelatine becomes insoluble where the light has acted, when I float this paper on hot water, those parts which have been acted upon by light ought to remain on the paper, and those parts which have not been acted on ought to dissolve, carrying the ink with them. I place the uncoated side of the paper on the boiling water, and I notice that an action takes place; where the light has not acted the gelatine is swelling up, showing that it is absorbing water; in other words, I see that the lines forming the image are depressed, and the gelatine around is in relief. I pour a gentle stream of water over the surface, and then I wash away the soluble parts by the application of a sponge. The lines are perfectly distinct, appearing black on a white ground. Both of these properties of chromated gelatine, which I have shown you, are utilised in what we call photolithography. The images formed in the greasy ink can be transferred to a lithographic stone and impressions taken in the ordinary manner. This last process is known as the Southampton method for preparing a photographic transfer for lithography. The first method I showed you is certainly equally as effective. It is also on these two properties of gela-

tine, when in contact with the dichromates—viz., non-absorption of water and insolubility where light has acted—that a variety of other photographic printing processes are

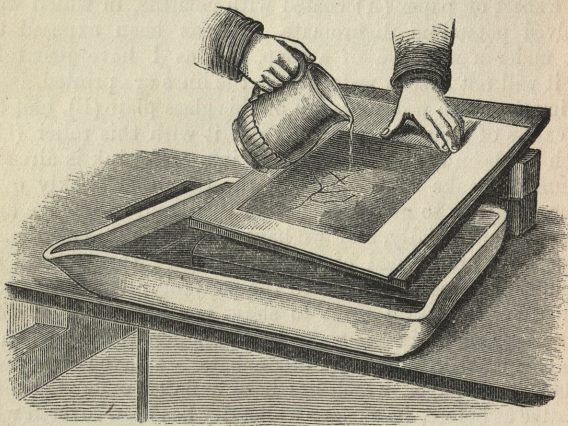


FIG. 9.

founded. On the later reaction is founded the autotype process, where the image is formed absolutely of coloured gelatine, all the parts not acted upon by light having dissolved away; whilst on the former are built up all those processes which produce prints in graduated tints of greasy ink after an image has been obtained on gelatine that has been hardened and rendered insoluble in water (though still leaving it capable of absorbing water in the parts not acted upon by light), by the addition of such substances as tannin, chrome alum, &c. As examples of such processes I may mention the heliotype, albertype, and autotype mechanical processes.

I have now come to the end of the time allotted to me, and I trust that the explanations as far as they have gone have been clear; but in treating of such a large subject as photography, it would be necessary for you to listen to me for as many days as you have hours, in order that I might enter into the details of much which I have merely been able to glance at.

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